Pressure- and Temperature-Variable Viscosity Dependencies of Rotational Correlation Times for Solitary Water Molecules in Organic Solvents (INTERFACE SCIENCE - Solutions and Interfaces)

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Pressure- and Temperature-Variable Viscosity Dependencies of Rotational Correlation Times for Solitary Water Molecules in Organic Solvents

Chihiro Wakai and Masaru Nakahara

^{2}H-NMR spin-lattice relaxation times T_1 have been measured for solitary water molecules (D_2O) at a low concentration in apolar and polar organic solvents (C_6H_6 , $CHCl_3$, and CH_3CN) at 30℃ at high pressures in order to obtain the rotational correlation times τ_{2R} . We have tested the two forms of modified Stokes-Einstein-Debye law; the linear and nonlinear forms are $\tau_{2R} = \tau_{2R}{}^0 + S(\eta/T)$ and $\tau_{2R} = B(\eta/T)^\alpha$, respectively. It is shown that the linear form is practically better, and that the nonlinear form constrained at $\eta/T = 0$ is invalid. The extended-diffusion models based on isolated binary collisions cannot be used to explain the observed pressure effect because of the neglect of the attractive solute-solvent interactions.

Keywords: Rotational friction/ Hydrodynamic model/ High-pressure NMR

The rotational correlation time τ_{2R} is often estimated in the framework of the Stokes-Einstein-Debye (SED) law based on the hydrodynamic model. As discussed previously [1, 2], the SED law is usually modified as follows. The linear form with an intercept is

$$\tau_{2R} = \tau_{2R}{}^0 + S(\eta/T), \quad (1)$$

and the nonlinear form without an intercept is

$$\tau_{2R} = B(\eta/T)^\alpha . \quad (2)$$

Here, h is the solvent viscosity, S and B are the constants, and a is the fractional viscosity exponent. As seen from Fig. 1, Eq. (1) is obviously superior to Eq. (2). The data fit to Eq. (2) is not natural but merely forced to pass the zero value of η/T. The zero-point constraint makes the fit curve (broken line) concave upward with a fractional power. The intercept is significantly larger with a smaller slope in the pressure-variable experiment than in the temperature-variable experiment. The large positive intercept in Eq. (1) gives rise to the fractional nature of the viscosity exponent in the fit to the form of Eq. (2).

Figure 2 illustrates the temperature- and pressure-variable density dependencies of τ2R. In the pressure-variable experiment, the dependencies are much larger than the prediction of the extended-diffusion model based on isolated two-body collisions. In the temperature-variable experiment, the τ_{2R} vs ρ_N curve rises very sharply in any system. This is mainly due to the kinetic effect which may be represented by an exponential factor of the Arrhenius type.

References

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INTERFACE SCIENCE — Solutions and Interfaces —

Scope of research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biochemical interests are systematically studied by NMR under extreme conditions. Simple and complex solution systems are supercooled, overheated, and compressed to high pressures to shed light on microscopic factors which control rotational and translational motions of ions and molecules. Vibrational spectroscopic studies are carried out to elucidate structure and orientations of organic and water molecules in ultra-thin films. Crystallization of protein monolayers, advanced dispersion systems at liquid-liquid interfaces, and biomembranes are also investigated.

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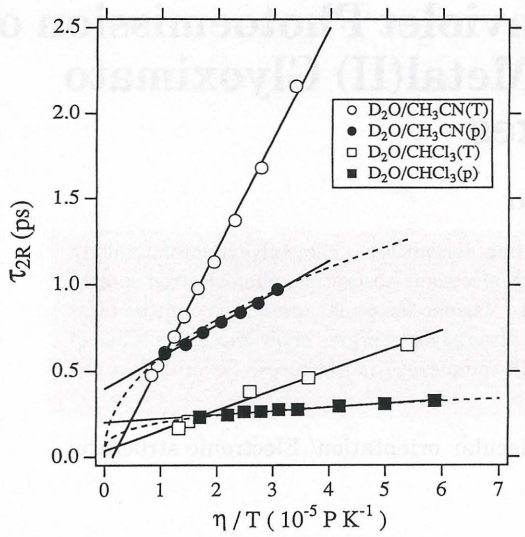

Figure 1. Plots of the rotational correlation times for D_2O in CH_3CN and $CHCl_3$ against solvent viscosity divided by temperature. Open and solid symbols are for temperature- and pressure-variable viscosity variations, respectively. Circles and squares denote D_2O/CH_3CN and $D_2O/CHCl_3$ systems, respectively.

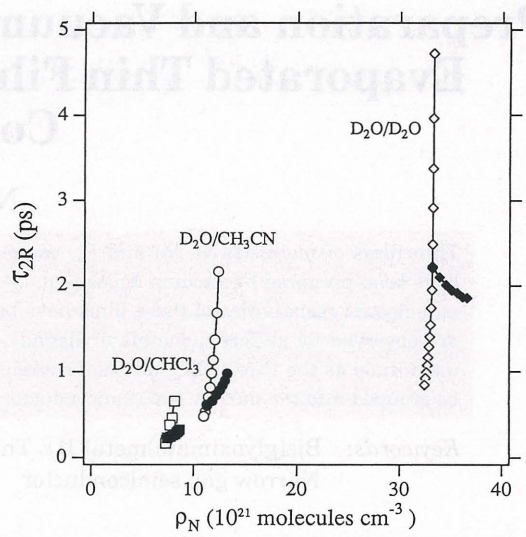

Figure 2. Plots of the rotational correlation times for D_2O in CH_3CN, $CHCl_3$, and pure liquid against the number densities (ρ_N) of the solvents for pressure- (solid symbols) and temperature-variable (open symbols) experiments.

Quantitative Analysis of Uniaxial Molecular Orientation in Langmuir-Blodgett Films by Infrared Reflection Spectroscopy

Takeshi Hasegawa, Satoshi Takeda, Akira Kawaguchi, and Junzo Umemura

A new method for calculating infrared reflection-absorbances of multilayered LB films with a uniaxial anisotropy around the surface normal was developed, to analyze optical properties and molecular orientations in ultrathin films.

Keywords: Molecular orientation/ Langmuir-Blodgett films/ FT-IR external reflection spectra/Uniaxial anisotropy

With this method, infrared external reflection spectra of a 9-monolayer Langmuir-Blodgett (LB) film of Cd stearate prepared on a GaAs substrate (Figure 1) were analyzed, and the tilting angle of the hydrocarbon chain was obtained as 14° from the surface normal, in fair agreement with that obtained by X-ray diffractometry. Reflection-absorption spectra of the same LB film on a silver-evaporated slide glass at various temperatures were also analyzed by the same method and the orientation angle of each molecular group was obtained, clarifying the process of disordering with the increase of temperature. Further, the dependence of the degree of disordering on the monolayer location in LB films were discussed in light of the isotope substitution experiment [1].

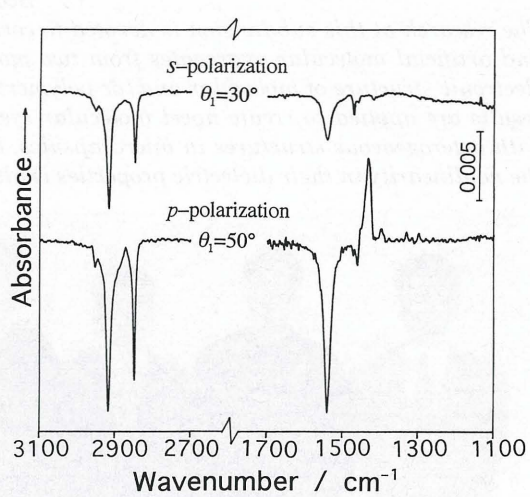

Figure 1. FT-IR external reflection spectra of 9-monolayer LB film of Cd stearate on GaAs.

References

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